

Heat of Formation of the CH₃CO Radical

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The heat of formation of the CH₃CO radical has been determined at high levels of theory using an isodesmic reaction. Our best value is -0.55 ± 0.6 kcal/mol at 0 K (or -2.2 ± 0.7 kcal/mol at 298 K), which supports the recent experimental value of Niiranen *et al.* over the many older values. The other bond energies in acetaldehyde are computed using the G2(MP2) approach.

Introduction

The heat of formation of the CH₃CO radical has been determined on several occasions¹⁻¹⁶ (see Table 1). The experimental literature before 1992 supports a value of about -5 kcal/mol for the heat of formation. Yadav and Goddard¹⁷ studied acetaldehyde and its dissociation using relatively low levels of theory. While the calculations illustrated the character of the potential energy surface, they were incapable of accurately determining the heat of formation of CH₃CO. The more accurate calculations of Francisco and Abersold¹⁵ support a heat of formation of around -5 kcal/mol, especially if one takes their value from scheme 1 (-4.9 kcal/mol) in preference to their average value. That is, their reaction which involves breaking a C-H bond is expected to be more accurate than their scheme which involved breaking a C-Cl bond, because it is easier to describe a C-H bond than a C-Cl bond. Also in 1991, Radom and co-workers¹⁶ computed the C-H bond energy in acetaldehyde using the G1 approach.¹⁸ Their bond energy (at 0 K) was 3.8 kcal/mol larger than the experimental value (derived from a heat of formation¹³ at 298 K of -5.4 kcal/mol). Because the G1 approach is usually accurate to ± 2 kcal/mol, they suggested that the acetyl radical heat of formation was several kcal/mol smaller in magnitude than experiment. Unfortunately, they did not pursue this suggestion as the acetyl radical was only a minor aspect of their study. Recently, Niiranen *et al.*¹⁴ determined a heat of formation of -2.39 ± 0.29 kcal/mol for CH₃CO from a kinetics study of the reaction CH₃CO + HBr. This value supports the suggestion of Radom and co-workers that the older values are too large in magnitude.

In this work we determine the heat of formation of CH₃CO using high levels of theory in conjunction with large basis sets. In addition, we determine all of the other bond energies in CH₃CHO using the G2(MP2) approach.¹⁹ The G2(MP2) approach combines a highly accurate method in small basis sets with a more approximate method in a large basis set and an empirical correction, and it is therefore a very cost effective method of computing bond energies accurate to about ± 2 kcal/mol.

Methods

In the first set of calculations, the G2(MP2) approach¹⁹ is used to compute all of the bond energies in CH₃CHO. In the second set of calculations, the CH₃CO-H bond energy is studied using the isodesmic reaction,



This reaction is studied at several levels of theory using the correlation consistent polarized valence triple-zeta (cc-pVTZ) sets of Dunning.²⁰ We use both spin-restricted and spin-

TABLE 1: Summary of the Heat of Formation (in kcal/mol) of CH₃CO at 298 K

Experiment	
acetone pyrolysis (1955) [1] ^a	-10.8
azomethane/CO photolysis (1958) [2]	-3.0
acetone pyrolysis (1962) [3]	-6.2, -6.3
photoionization mass spectroscopy (1964) [4]	-6.5
azomethane/CO photolysis (1965) [5]	-4 \pm 2
spectrophotometric technique (1966) [6]	-6.3 \pm 2.0
spectrophotometry (1966) [7]	-5.4 \pm 0.8
biacetyl pyrolysis (1969) [8]	-5.1 \pm 2.0
calorimetry (1969) [9]	-5.8 \pm 0.4
electron impact (1969) [10]	-2 \pm 5
shock tube studies of ketone (1984) [11]	-3.3
electron impact/mass spectrometry (1984) [12]	-4.5
photoelectron spectroscopy (1989) [13]	-5.4 \pm 2.1
kinetics (1992) [14]	-2.39 \pm 0.29
Theory	
MP2/MP4 (1991) [15]	-4.2 \pm 2
G1 (1991) [16]	-1.8 \pm 2 ^b
G2 present work	-1.8 \pm 2
best estimate present work	-2.2 \pm 0.7

^a Numbers in brackets are reference numbers. ^b Computed using the reported C-H bond energy at 0 K and our correction to 298 K.

unrestricted Hartree-Fock (RHF and UHF, respectively) reference wave functions. Correlation is added to both reference wave functions using second-order Møller-Plesset perturbation theory²¹ (MP2) and the coupled cluster single and double excitation approach²² including a perturbational estimate of the triple excitations,²³ which is denoted CCSD(T). We precede these methods with an "R" or a "U" to indicated that an RHF or UHF reference is used. This notation shows how the open-shell calculations are performed, as the closed-shell calculations are always RHF based. For the UHF reference, we also use the quadratic configuration interaction method²⁴ including a perturbational estimate of the triple excitations [QCISD(T)]. To study the effects of one-particle basis set saturation, the RMP2 level of theory is also considered using the cc-pV quadruple-zeta (cc-pVQZ) basis sets.²⁰

For the study of reaction 1, the geometries are obtained at the UMP2 level of theory using the 6-311+G(3df,2p) basis set.²⁵ The vibrational frequencies are obtained at the same level of theory; the zero-point correction is computed as 0.98 times one-half the sum of these MP2 frequencies. This scaling factor is based on the observation of Grev, Janssen, and Schaefer²⁶ that averaging half the sum of the fundamentals and half the sum of the harmonic frequencies yields a much better approximation to the zero-point energy, and our observation²⁷ that 0.96 times the MP2 frequencies computed using the 6-311+G(3df,2p) basis set yields good agreement with the experimental fundamentals for CH₃OH and CH₂OH.

We adopt a C-H bond energy for methane of 103.35 ± 0.2 kcal/mol. This value is consistent with the value (103.24 ± 0.12

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TABLE 2: G2(MP2) Bond Energies (in kcal/mol) for Acetaldehyde at 0 K

	G2(MP2)	G1 ^a
CH ₃ CHO → CH ₃ CO + H	88.74	88.7
CH ₃ CHO → CH ₂ CHO + H	95.92	95.6
CH ₃ CHO → O(³ P) + CH ₃ CH(³ A'')	186.56	
CH ₃ CHO → CO + CH ₄	-7.60 ^b	-6.9
CH ₃ CHO → HCO + CH ₃	83.51	84.1

^a Reference 16. ^b The experimental value³¹ is -6.03 kcal/mol.

kcal/mol) determined by Chupka²⁸ from the photoionization spectrum of methane and the value deduced (103.45 ± 0.1 kcal/mol) from the CH₃ heat of formation at 298 K by Dobis and Benson²⁹ from the reaction of methane with Cl. It is also consistent with the C-H bond energy for CH₄ deduced (103.2 ± 0.3 kcal/mol) from the CH₃ heat of formation by Russell *et al.*³⁰

The heat of formation of CH₃CO is computed using the known³¹ heats of formation of CH₃CHO and H and the heat of reaction 1. The heat of formation is corrected to 298 K using our computed vibrational frequencies, except for the torsion of the CH₃ group, which is treated as a hindered rotor following Pitzer and co-workers.³² The barrier is computed following the ideas of the G2(MP2) approximation: (1) the equilibrium and saddle point geometries are optimized at the MP2 level of theory using a 6-31G* basis set; (2) at these geometries, using the 6-311G** basis set, the energies are computed using the QCISD(T) method; and (3) these QCISD(T) energies are corrected for basis set limitations using the difference in the MP2 energies between the 6-311G** and 6-311+G(3df,2p) basis sets.

The calculations were performed using ACES II,³³ Gaussian 90,³⁴ Gaussian 92,³⁵ or DISCO³⁶ on the NASA Ames Central Computing Facility or NAS CRAY C90 computers or on the Computational Chemistry IBM RS/6000 computers.

Results and Discussion

We first consider all the bond energies in acetaldehyde—see Table 2. There is very good agreement between the G1 and G2(MP2) levels of theory. As the heats of formation of CO and CH₄ are well-known,³¹ we can compare our result for this dissociation pathway with experiment. The G2(MP2) result differs with experiment by 1.6 kcal/mol, which is within its estimated accuracy of ±2 kcal/mol. The G1 result is in slightly better agreement with experiment. The calculations show that the methyl hydrogen is about 7 kcal/mol more strongly bound than the aldehyde hydrogen. We also find that it takes about 5 kcal/mol more energy to remove the aldehyde hydrogen than the methyl group. As expected, the C-O double bond is quite strong. The G2(MP2) results support the suggestion¹⁶ that the CH₃CO heat of formation is not ≈ -5 kcal/mol. However, as the comparison of experiment with the G2(MP2) result for dissociation to CO + CH₄ shows, a more accurate calculation is required to definitively determine the CH₃CO heat of formation.

In Table 3 we summarize the heat of reaction 1. The UHF and RHF results are very similar, differing by only 0.26 kcal/mol. The difference between the UMP2 and the RMP2 results is larger, -0.63 and 0.73 kcal/mol, for the ACES II and DISCO implementations, respectively, but these differences are smaller than that (1.36 kcal/mol) between the two RMP2 implementations. At higher levels of theory the agreement between the RHF and UHF based approaches is very good; for example the difference between the RCCSD(T) and UCCSD(T) results is only 0.06 kcal/mol. Note that the QCISD(T) result is very similar to the RCCSD(T) and UCCSD(T) results. Because the DISCO implementation of RMP2 agrees very well with the CCSD(T) results, we apply this level of theory to the larger cc-pVQZ basis set. This leads to only a small change in heat of reaction.

Our best estimate for the heat of reaction 1 is -16.92 kcal/mol. We obtain this by correcting the RCCSD(T) result from the

TABLE 3: Heat of Reaction for CH₃ + CH₃CHO → CH₄ + CH₃CO and the Aldehyde C-H Bond Energy (in kcal/mol)

	heat of reaction without zero-point	C-H bond energy ^a
cc-pVTZ Basis Set		
UHF	-10.86	94.28
UMP2	-17.27	87.86
QCISD	-16.20	88.94
QCISD(T)	-16.96	88.18
UCCSD	-15.66	89.48
UCCSD(T)	-16.74	88.39
RHF	-10.60	94.54
RMP2(ACES II ^b)	-17.90	87.24
RMP2(DISCO ^c)	-16.54	88.60
RCCSD	-15.58	89.56
RCCSD(T)	-16.80	88.34
cc-pVQZ Basis Set		
RHF	-10.63	94.50
RMP2(DISCO)	-16.66	88.48

^a The computed heats of reaction are corrected for zero-point effects (1.79 kcal/mol) using the scaled (0.98) MP2 frequencies. The experimental C-H bond energy in CH₄ is taken to be 103.35 kcal/mol, see text. ^b Indicates that the ACES II³³ implementation of RMP2 is used. ^c Indicates that the DISCO³⁶ implementation of RMP2 is used.

cc-pVTZ basis set with the change in the RMP2 results between the cc-pVTZ and cc-pVQZ basis sets. Because of the small (0.12 kcal/mol) change between the cc-pVTZ and cc-pVQZ basis sets, we suspect that further basis set saturation will make only a small change in the result. The small change in bond energy between the CCSD and CCSD(T) levels of theory suggests that we are near the *n*-particle limit. Because of the modest-sized effect of electron correlation, the small effect of triple excitations, and the small change in the MP2 results with basis set improvement, we estimate that our computed heat of reaction (without zero-point effects) is accurate to ±0.2 kcal/mol.

The zero-point contribution to the reaction is computed to be 1.79 kcal/mol using the scaled MP2 frequencies—see Table 4. An alternative value of 1.95 kcal/mol is obtained from the scaled (0.91²⁶) 6-31G* SCF frequencies. We use the MP2 results but take the difference between the two approaches as a measure of the uncertainty in our value. Combining this with our best estimate for the heat of reaction 1 and the experimental C-H bond energy in CH₄ yields an aldehyde C-H bond energy of 88.22 ± 0.6 kcal/mol, where the uncertainty reflects our estimates for the uncertainty in the heat of reaction 1 (0.2 kcal/mol), the uncertainty in the zero-point correction (0.16 kcal/mol), and the uncertainty in the CH₄ bond energy (0.2 kcal/mol). Since the first two quantities are only estimates, we add all three together to compute our estimated uncertainty are only estimates, we add all three together to compute our estimated uncertainty in the bond energy. It is interesting to note that the G2(MP2) bond energy is in good agreement with our best estimate.

When we compute the correction to 298 K, we treat the CH₃ motion as a hindered rotation. We therefore compute the barrier for this rotation. For CH₃CHO in the 6-311G** basis set, we find a barrier of 1.173 and 1.106 kcal/mol at the MP2 and QCISD(T) levels of theory, respectively. The MP2 results in the larger 6-311+G(3df,2p) basis set is 1.128 kcal/mol. Correcting the QCISD(T) result with the difference between the MP2 results leads to our best estimate of 1.06 kcal/mol for the barrier to CH₃ rotation. For CH₃CO our best estimate for the barrier is 0.48 kcal/mol, which is derived from the computed barriers of 0.419, 0.371, and 0.526 kcal/mol, for the MP2, QCISD(T), and MP2-(6311+G(3df,2p)) levels of theory, respectively. We compute 0.4095 and 0.3413 kcal/mol for the contribution of this rotation to *H*^o₂₉₈ - *H*^o₀ for CH₃CHO and CH₃CO, respectively. We treat the remaining modes as harmonic oscillators, leading to the total correction given in Table 5.

Using our best estimate for the C-H bond energy and the known³¹ heats of formation for CH₃CHO and H, we compute a

TABLE 4: Summary of the Geometrical Parameters Computed at the MP2 Level in the 6-311+G(3df,2p) Basis Set,^a and Unscaled MP2 Frequencies

degree of freedom	CH ₃ CHO	CH ₃ CO
C ₁ -O	1.210	1.182
C ₁ -C ₂	1.494	1.501
C ₁ -H _d	1.105	
C ₂ -H _a	1.084	1.088
C ₂ -H _{b,c}	1.089	1.086
∠C ₂ C ₁ O	124.5	128.6
∠OC ₁ H _d	115.5	
∠C ₁ C ₂ H _a	110.8	111.2
∠C ₁ C ₂ H _{b,c}	109.4	108.4
H _b C ₂ C ₁ O	121.6	121.8
a'		
ω ₁ C-H stretch	3215	3196
ω ₂ C-H stretch	3084	3088
ω ₃ C-H _d stretch	2965	
ω ₄ C-O stretch	1787	1936
ω ₅ CH ₃ deformation	1485	1485
ω ₆ C-H _d bend	1435	
ω ₇ CH ₃ deformation	1394	1374
ω ₈ C-C stretch	1147	1070
ω ₉ CH ₃ rock	910	897
ω ₁₀ C-C-O bend	510	471
a''		
ω ₁₁ C-H stretch	3164	3201
ω ₁₂ CH ₃ deformation	1494	1482
ω ₁₃ CH ₃ rock	1140	966
ω ₁₄ C-H _d bend	781	
ω ₁₅ torsion	160	109

^a The bond lengths are in Å and the angles in degrees. C₁ is the carbon bonded to the oxygen, while C₂ is the methyl carbon. H_a, for n = a, b, and c are the three methyl H atoms, while H_d is the remaining H atom. H_a and H_d are in the plane of the carbons and oxygen and H_b and H_c are the equivalent H atoms above and below this plane. Both molecules have C_s symmetry.

TABLE 5: Thermodynamic Quantities Used in This Work^a

molecule	ΔH° ₀	ΔH° ₂₉₈	H° ₂₉₈ - H° ₀
H	51.626	52.095	1.481
CH ₃ CHO	-37.139	-39.720	3.043 ^b
CH ₃ CO ^b	-0.55	-2.20	2.957

^a All values are in kcal/mol and are taken from ref 31 unless otherwise noted. ^b Present work.

heat of formation for CH₃CO of -0.55 ± 0.6 kcal/mol at 0 K. We correct this to -2.20 ± 0.7 kcal/mol using our computed $H^\circ_{298} - H^\circ_0$ values summarized in Table 5. We have increased in uncertainty by 0.1 kcal/mol to account for limitations of this correction. For example, the computed $H^\circ_{298} - H^\circ_0$ value for CH₃CHO is 0.03 kcal/mol smaller than that given by Wagman *et al.*³¹ Also the computed value for CH₃CO would be 0.11 kcal/mol larger if all modes were treated as vibrations rather than treating the CH₃ torsion as a hindered rotation.

Conclusions

Our best estimate of -2.2 ± 0.7 kcal/mol for the heat of formation of CH₃CO is in excellent agreement with the experimental value (-2.39 ± 0.29 kcal/mol) determined by Niiranen *et al.*¹⁴ Because we have made conservative estimates of the errors in our computed results, we believe that, in spite of the

large number of values, we can rule out all the heats of formation below -3.0 kcal/mol.

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